Direct Correlation between Tc and CuO_2 Bilayer Spacing in $YBa_2Cu_3O_{7-x}$

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Abstract

We report the effects of epitaxial strain and deoxygenation on high quality $[YBa_2Cu_3O_{7-x}(YBCO)_N$ / $PrBa_2Cu_3O_7$ $(PBCO)_5]_{1000Å}$ superlattices, with $1 < N < 12$ unit cells. High spatial resolution electron energy loss spectroscopy (EELS) shows that strained, fully oxygenated YBCO layers are underdoped. Irrespective of whether underdoping is induced by strain or deoxygenation, X-ray diffraction analysis shows that Tc correlates directly with the separation of the CuO_2 bilayers.

Since the discovery of the high Tc superconductivity, the relation between critical temperature and structure has been the focus of considerable interest. Changes in the critical temperature (Tc) induced by pressure (physical) and isovalent substitution (chemical pressure) have been extensively investigated to find which interatomic distances within the unit cell are relevant for the mechanism of superconductivity (see for instance references 1-3 and references therein). However, despite a considerable experimental and theoretical effort, a definitive answer has not yet been obtained, partly due to the complex intracell structure of the cuprates. Most theories consider superconductivity primarily located on the CuO_2 planes, which are coupled by proximity or pair tunneling effects [4-9], and extensive experimental work has been done, directed to examine the importance of the distance between CuO_2 planes of the same and of neighboring cells for the mechanism of superconductivity. Modifications of the interlayer coupling have been explored changing the number of copper planes [10], their inner structure [11,12], or intercalating non superconducting spacers as iodized compounds [13] or organic spacers [14].Concerning the separation between neighboring CuO_2 planes, substitution of the rare earth element is known to influence lattice dimensions (chemical pressure experiments) [1, 15]. An increase of the rare earth ionic radius from 0.99 A for Yb to 1.08 for Nd is known to increase the distance between planes and also Tc from 88 to 95 K [16]. Despite the extensive work, the results of some of the experiments are contradictory[13,14], a clear picture has not emerged yet. Changes in the distance between planes, or modifications in the intracell distances due to cationic substitution, may have, in addition, a direct influence in the charge transfer and thus on the carrier concentration.On the other hand it is well known that changes in oxygen content, which result in changes in the carrier concentration, also cause significant structural changes [17,18]. This interplay between structural changes and doping has obscured the relationship between superconductivity and structure.

In addition to physical or chemical pressure, structural changes induced by epitaxial strain in thin films can be used to explore the relationship between structure and superconductivity. In a previous paper we have reported that significant epitaxial strain occurs in

ultrathin $YBa_2Cu_3O_{7-x}$ layers in $[YBa_2Cu_3O_{7-x}(YBCO)_N$ / $PrBa_2Cu_3O_7$ $(PBCO)_5]_{1000Å}$ superlattices, with N ranging between 1 and 12 unit cells, as a result of a 1% in-plane lattice mismatch with PBCO. This epitaxial strain causes non-uniform changes in the interatomic distances within the unit cell which correlate with the decrease of the critical temperature in the strained layers [19,20].

In this paper we compare structural changes resulting from epitaxial strain with those arising from doping in oxygen depleted YBCO samples. In both cases, changes in the intracell distances are comparable in magnitude but some have opposite signs, and the comparison provides important information on the interplay between structure and superconducting properties. Using high spatial resolution electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) we show, for the first time, that epitaxially strained layers are underdoped. Structure refinement by X-ray diffraction shows that regardless of whether underdoping is caused by strain or deoxygenation, Tc is uniquely determined by the CuO_2 bilayer separation. No other intracell spacings show such a correlation, indicating that the CuO_2 bilayer spacing is the fundamental structural signature of Tc in the superconducting cuprates.

The samples for this study were epitaxially strained $[YBa_2Cu_3O_{7-x}$ $/PrBa_2Cu_3O_7]_{1000Å}$superlattices grown by high pressure (3.4 mbar) oxygen sputtering on (100) $SrTiO_3$ substrates, held at 900^oC. The PBCO layer thickness was fixed in 60 Å, (5 unit cells), enough to decouple the superconducting layers, while the YBCO layer thickness ranged between 12 and 1 unit cells. The number of bilayers grown in the stacking was adjusted to obtain samples 1000Å thick. Structure was analyzed by x-ray diffraction (XRD) and refined with the SUPREX software [21,22], which allows refinement of atomic positions in the c- direction within the unit cell. Electron energy loss spectroscopy (EELS) measurements and Z-contrast images were obtained in a VG Microscopes HB501UX STEM operated at 100kV with a field emission gun, and a parallel detection EELS post-column spectrometer. An anular dark field detector was used for imaging. In this microscope, the electron probe can be focused down to a diameter of a 2.2Å. Cross section samples for STEM were

prepared by conventional grinding, dimpling and ion milling with Ar ions with an energy of 5 kV, at an incidence angle of 7^o. Final cleaning was done at low voltage of 2 kV.

Superlattices grown by this technique had atomically flat interfaces with negligible interdiffusion as proven by x-ray diffraction analysis and energy filtered transmission electron microscopy. Details about sample preparation and interface characterization can be found elsewhere [20,23]. In these YBCO layers, when the thickness is reduced below 4 unit cells epitaxial strain effects arise due to the 1% lattice mismatch between YBCO and PBCO, causing a quite inhomogeneous reorganization of intracell distances [19]. For the thinnest (one unit cell) YBCO layer, the CuO_2 planes move closer to each other by 4%, while the Ba ion approaches the CuO chains by 4% but moves away from the CuO_2 planes by 2%. Results for several sets of samples are shown in Fig. 1. Tc is plotted versus the distance between the CuO_2 planes and the Y cation, i.e. half of the distance between adjacent CuO_2 planes (fig 1a), and versus the distance between the Ba ion and the CuO chains (fig 1b). Note that despite the strain within the single layers might be inhomogeneous, x-ray analysis supplies values for the intracell distances averaged over the whole layer. The $[YBCO_N/PBCO_5]$ superlattice samples, with 1<N<12 unit cells, where the parameter tuning the Tc is epitaxial strain, are represented by solid squares. The c-lattice parameter of the PBCO was constant at a value of 11.71 $\mathring{\mathbf{A}}$, very close to the bulk value, pointing to an unstrained structure of the PBCO [19]. Lattice distortion due to the lattice mismatch with the STO in the first PBCO layer (+0.4 % along a axis and -0.6 % along b axis) was not detected.

It is interesting to compare these structural changes with those arising through deoxygenation of bulk YBCO by Jorgensen et al [17]. Upon oxygen depletion the hole density decreases gradually, and so does the value of Tc. At the same time, quite substantial structural changes occur within the bulk YBCO unit cell. Contrary to the strained samples, one observes that as oxygen is removed, the Ba ion moves *away* from the basal CuO chain (5% for an oxygen content of 6.4 per formula unit), while the CuO_2 planes *approach* each other (3%). Meanwhile, the distance between the Ba ion and the CuO_2 planes decreases slightly. Figure 1 demonstrates a clear correlation between structural changes and variations in the critical

temperature for both deoxygenation and epitaxial strain. It is remarkable that changes in the different intracell distances caused by strain and deoxygenation are quantitatively similar, although in the case of the Ba-CuO distance show opposite sign.

For the superlattices, increasing epitaxial strain decreases the distance between CuO_2 planes, as would be expected from the Poisson effect alone. This is true both for adjacent planes (same cell) and for planes of neighboring cells [19,20]. It would be expected that the enhanced coupling would increase Tc, which is contrary to the results observed. This suggests that a different effect is ruling the changes in the critical temperature. Significantly, the spacing of the CuO_2 bilayers *decreases also upon oxygen removal*, despite the fact that the c lattice parameter increases in this case.

The behavior of the Ba-CuO spacing between the Ba atom and the CuO chains (figure 1b) is more complicated. In epitaxially strained samples Tc decreases with decreasing Ba-CuO separation, while the opposite trend is found for the oxygen depleted bulk samples. The bell shaped aspect of figure 1b could point at first glance to an optimal Ba-CuO distance for which the maximum Tc is attained. Since on the right branch, the oxygen depleted samples, Tc decreases due to underdoping, the left branch, would be interpreted as overdoping of the CuO_2 planes due to the strain induced structural change. However, this conclusion is opposite to that indicated by the contraction of the CuO_2 bilayer spacing which occurs both for strained and for underdoped samples. In the following we explicitly deoxygenate the strained superlattices to show that overdoping is *not* the cause of the reduced Tc.

Strained $[YBCO_1/PBCO_5]_{1000\text{Å}}$ superlattices were depleted of oxygen to a nominal content 7-x= 6.93, 6.8 and 6.6 per formula unit. Oxygen content was adjusted *in-situ*, after sample growth, following a stability line in the phase diagram corresponding to the desired oxygen stoichiometry during sample cool down [24]. These oxygen contents are nominal and the values were inferred from the results obtained on companion thin films of YBCO which were given the same deoxygenation sequence [25]. The structure was quantitatively determined through the refinement of the x-ray diffraction spectra. When oxygen was removed, the superlattice Bragg peaks shifted to lower angles, denoting a monotonic increase of the c

lattice parameter. Although a direct measure of the oxygen content in our superlattices is not possible, the relative change in the c lattice parameter obtained from x ray analysis of the superlattices was in perfect agreement with the values found for bulk samples with the same nominal compositions.

Figure 2 shows changes of various intracell distances in the superlattices versus the nominal oxygen content. Results (obtained from x-ray refinement) are shown for the distance from the CuO_2 planes to the Y atom (Y-CuO_2), from the CuO_2 planes to the Ba ion (CuO_2-Ba), and from the Ba ion to the chains (Ba-CuO). Deoxygenated superlattices (solid symbols) follow precisely the same trend as neutron data for bulk samples (open symbols) from reference [17]. This shows that the structural changes caused by deoxygenation in strained layers track exactly those occuring in (relaxed) bulk samples. We can therefore directly test the correlation of the Ba-CuO spacing to Tc. For a nominal oxygen content of 7-x = 6.6, we have Tc = 10K in the strained superlattice (see figure 3, discussed below) and the Ba-CuO spacing attains a value of 2.14Å. This is close to the value found for optimally doped *unstrained* YBCO with Tc = 90 K (see figure 1b). It can be concluded that Tc is *not* determined by the absolute value of the Ba-CuO spacing.

We now present definitive evidence that the strained superlattices are underdoped. Figure 3 shows the resistance curves corresponding to the deoxygenated $[YBCO_1/PBCO_5]_{1000Å}$ superlattices. The dotted line corresponds to the fully oxygenated $[YBCO_1/PBCO_5]$ superlattice, and the dashed lines correspond to 7-x = 6.8 and 7-x = 6.6 *in-situ* deoxygenated samples. Slight deoxygenation was also conducted by *ex-situ* annealing the fully oxygenated $[YBCO_1/PBCO_5]$ superlattices at 125^oC in N_2 atmosphere for succesive half hour intervals (solid lines in figure 3) [25]. XRD spectra corresponding to these samples did not show measurable structural changes. When decreasing oxygen content we can observe how resistance increases while the Tc decreases smoothly. The reduction in Tc upon deoxygenation clearly shows that the samples are not overdoped in their strained, fully oxygenated state.

This result is confirmed using high spatial resolution EELS. Fine structure on the oxygen K-edge provides a sensitive measure of the superconducting carrier concentration [26-29].

It is known that the Cu-3d and O-2p states of the CuO_2 plane atoms lie close to the Fermi level. As a result of the dipole selection rule, the unoccupied part of these states can be investigated by exciting transitions from Cu-2p and O-1s levels - in other words, by examining the fine structure of the copper L_{23} and oxygen K edges. In fully oxygenated YBCO two pre-edge features develop at the O-K edge: a shoulder around 535 eV, which represents transitions to unoccupied Cu-3d states, and a peak around 528 eV representing transitions to O-2p states which give rise to holes in the valence band [26-29]. In samples where the oxygen content is decreased this last peak falls in intensity, indicating a decrease in hole concentration and a reduction in the critical temperature. In figure 4 we show the energy loss spectra corresponding to the O-K edge for two different superlattices: a relaxed [$YBCO_8/PBCO_5$] sample, with a Tc of 88K (dotted line) and a strained [$YBCO_1/PBCO_5$] sample, showing a Tc of 35K (solid line). Spectra were acquired placing the electron probe on the center of the YBCO unit cell. The inset of figure 4 displays a Z-contrast image of a [$YBCO_1/PBCO_5$] sample showing very good resolution of the one unit cell thick layers. While the pre-peak at 528 eV is present for the relaxed sample, it is absent in the ultrathin strained layers. This evidences an important change in the hole density in the YBCO layers in the strained superlattice, confirming that the hole concentration is substantially reduced in epitaxially strained samples. Therefore, we can rule out the possibility of overdoping due to strain as a cause of Tc depression in [$YBCO_1/PBCO_5$] superlattices. It is possible that the strained layers are underdoped not due to the strain but as a result of oxygen deficiency provided that the determination of absolute oxygen concentration in such thin films is a difficult task. However, annealings in pure oxygen at 1 atmosphere and 500 ^oC did not produce significant T_c changes. Moreover, these fully oxygenated samples did not show measureable persisting photoconductivity after long term illumination with white light [30], thus excluding the possibility of oxygen deficiency.

Having established that both epitaxially strain and deoxygenation cause underdoping, we return to the correlation of the CuO_2 bilayer separation with Tc shown in Fig. 1a. For our samples this correlation is *independent* of how a particular spacing was achieved,

epitaxial strain or deoxygenation (or a combination). This shows that *the primary structural signature of doping level and Tc is the CuO_2 bilayer spacing.* This can be interpreted naively as follows: as oxygen is removed from the chains, electrons are returned to the CuO_2 planes, which are therefore more strongly attracted by the trivalent rare earth ion. In underdoped samples the separation of the CuO_2 planes is thus reduced.Our results do not rule out the posibility of other effects such as fluctuations or size effects being involved in the Tc depression in ultrathin films [31-35] . But we report new experimental results showing the connection between Tc and structural modifications.

In summary, we have examined the interplay between epitaxial strain and doping in strained $[YBa_2Cu_3O_{7-x}(YBCO)_N$ / $PrBa_2Cu_3O_7$ $(PBCO)_5]_{1000Å}$ superlattices. Through resistivity measurements and high spatial resolution EELS we have shown directly that strained ultrathin layers are underdoped. Deoxygenation of strained samples causes non-uniform changes in the intracell structure, following trends quantitatively and qualitatively similar to those observed in deoxygenated bulk YBCO. In all cases Tc is directly related to the separation of the CuO_2 bilayers. In contrast, the distance between the Ba atom and the basal plane behaves quite differently with epitaxial strain and doping and can therefore be used to monitor the interplay between them. These results should stimulate future theoretical studies to highlight the role played by the Ba atom position on the charge transfer mechanism.

REFERENCES

[1] A. A. R. Fernandes, J. Santamaria, S. L. Bud´ko, O. Nakamura, J. Guimpel, I. K. Schuller, Phys. Rev. B **44**, 7601 (1991)

[2] J. P. Attfield, A. L. Kharlanov, J. A. McAllister, Nature **394**, 157 (1998)

[3] W.E. Pickett. Phys. Rev. Lett. **78,** 1960 (1997)

[4] S. Chakravarty, A. Sudbø, P.W. Anderson, S. Strong, Science **261**, 337 (1993),

[5] S. Chakravarty, A. Sudbø, P.W. Anderson, S. Strong Phys. Rev. B **49,** 12245 (1994)

[6] S. Chakravarty and P.W. Anderson, Phys. Rev. Lett. **72,** 3859 (1994)

[7] P.W. Anderson, Science, **279,** 1196 (1998)

[8] A.J. Legget Science, **274**, 587 (1996)

[9] J.L. Tallon, G. V. M. Williams, C. Bernhard, D. M. Pooke, M.P. Staines, J.D. Johnson, R.H. Meinhold. Phys. Rev. B **53**, R11972 (1996)

[10] Xiaojia Chen, Chande Gong. Phys. Rev. B **59** 4513 (1999)

[11] O. Chmaissem, J.D. Jorgensen, S. Short, A. Knizhnik, Y. Eckstein, H. Shaked. Nature, **397** 45 (1999)

[12] K.A. Lokshin, D.A. Pavlov, S.N. Putilin, E.V. Antipov, D.V. Sheptyakov, A.M. Balagurov. Phys. Rev. B **63** 064511 (2001)

[13] X.D. Xiang, W.A. Vareka, A. Zettl, J.L. Corkill, M.L. Cohen, N. Kijima, R. Gronsky. Phys. Rev. Lett. **68** 530 (1992)

[14] J.-H. Choy, S.-J. Kwon, G.-S. Park. Science **280** 1589 (1998)

[15] X.J. Chen, C.D. Gong, Y.B. Yu. Phys. Rev. B **61**, 3691 (2000)

[16] J.G. Lin, C.Y. Huang, Y.Y. Xue, C.W. Chu, X.W. Cao, J.C. Ho. Phys. Rev. B **51** R12900 (1995)

[17] J.D. Jorgensen, S. Pei, P. Lightfoot, D. G. Hinks, B. W. Hinks, B. W. Veal, B. Dabrowski, A.P. Paulikas, R. Kleb, Physica **C 171,** 93 (1990)

[18] C.C. Almasan, S:H. Han, B.W. Lee, L.M. Paulius, M.B. Maple, B.W. Veal, J.W. Donwey, A.P. Paulikas, Z. Fisk, J.E. Schirber, Phys.Rev. Lett. **69,** 680 (1992)

[19] M Varela, Z. Sefrioui, D. Arias, M.A. Navacerrada, M.A. López de la Torre, M. Lucia, C. Leon, G.D Loos, F Sanchez-Quesada, J Santamaria. Phys. Rev. Lett. **83,** 3936 (1999)

[20] M. Varela, D. Arias, Z. Sefrioui, C. León, C. Ballesteros, J. Santamaría. Phys. Rev. B **62,** 12509 (2000)

[21] E. E. Fullerton, I. K. Schuller, H. Vanderstraeten, Y. Bruynseraede, Phys. Rev. B **45**, 9292 (1992)

[22] E.E. Fullerton, J. Guimpel, O. Nakamura, I.K. Schuller, Phys.Rev. Lett. **69,** 2589 (1992).

[23] M. Varela, W. Grogger, D. Arias, Z. Sefrioui, C. León, C. Ballesteros, K. M. Krishnan, and J. Santamaría. Phys. Rev. Lett. **86**, 5156 (2001)

[24] Z. Sefrioui, D. Arias, M. Varela, J.E Villegas, M.A. López de la Torre, C. León, G. D. Loos, J. Santamaría.Phys. Rev. B **60,** 15423 (1999)

[25] It is important to note that while these soft anneals do not cause deoxygenation in single YBCO films, slight deoxygenation is favored in superlattices by the strained structure of the ab plane.

[26] N. Nücker, J. Fink, J.C. Fuggle, P.J. Durha, W. M. Temmerman. Phys. Rev. B **37,** 5158 (1988)

[27] N.D. Browning, J. Yuan, and L.M. Brown, 1992. *Physica C* **202**, 12 (1992)

[28] N.D. Browning, M.F. Chisholm, D.P. Norton, D.H. Downdes, and S.J. Pennycook, *Physica C* **212**, 185 (1993)

[29] N.D. Browning, J.P. Buban, P.D. Nellist, D.P. Norton, and S.J. Pennycook. *Physica C* **294**, 183 (1998)

[30] G. Nieva, E. Osquiguil, J. Guimpel, M. Maenhoudt, B. Wuyts, Y. Bruynseraede, M. B. Maple and I. K. Schuller, Appl. Phys. Lett. **60** 2159 (1992).

[31] C. Bandte. Phys. Rev. B **49** 9064 (1994)

[32] M. Rasolt, T. Edis, Z. Tesanovic. Phys. Rev. Lett. **66** 2927 (1991)

[33] Y. Matsuda, S. Komiyama, T. Terashima, K. Shimura. Y. Bando. Phys. Rev. Lett. **69** 3228 (1992)

[34] T. Terashima, K. Shimura. Y. Bando, Y. Matsuda, A. Fujiyama, S. Komiyama. Phys. Rev. Lett. **67** 1362 (1991)

[35] M.Z. Cieplak, S. Guha, S. Vadlamannati, T. Giebultowicz, P. Lindenfeld. Phys. Rev. B **50** 12876 (1994)

FIGURE CAPTIONS

Figure 1: (a) Tc of YBCO versus the CuO_2 bilayer separation, i.e., half the distance between adjacent CuO_2 planes (b) Tc versus the distance between the Ba ion and the CuO chains. Open circles are neutron diffraction data for deoxygenated bulk YBCO from reference [17]. Black squares represent the [$YBCO_N/PBCO_5$] superlattices with 12>N>1 unit cells. Open squares correspond to deoxygenated [$YBCO_1/PBCO_5$] superlattices. Dotted lines are a guide to the eye. Vertical dotted lines correspond to spacings in fully oxygenated bulk samples. Error bars denote the range within the XRD refinement was not sensitive to changes in the distances.

Figure 2: Changes ($d-d_0$) of various intracell distances versus the nominal oxygen content, where $d_0$corresponds to the fully oxygenated bulk samples. Superlattice results (obtained from x ray refinement) are shown for the Y-CuO_2 spacing (solid triangles), the CuO_2-Ba spacing (solid squares), and the Ba-CuO spacing (solid circles). Neutron diffraction data for bulk deoxygenated YBCO are taken from reference [17] (same notation but open symbols).

Figure 3: Resistance versus temperature curves corresponding to the set of deoxygenated [$YBCO_1/PBCO_5$] strained superlattices. The dotted line corresponds to a fully oxygenated strained sample. Dashed lines correspond to nominal oxygen contents of 7-x = 6.8 and 7-x = 6.6. Solid lines represent the set of slightly deoxygenated superlattices obtained by ex situ annealings at 125 ^{o}C.

Figure 4: Electron energy loss spectra corresponding to the O-K edge for two different superlattices: a relaxed [$YBCO_8/PBCO_5$] sample (dotted line) and a strained [$YBCO_1/PBCO_5$] sample (solid line). The vertical line shows the position of the pre-peak in the near edge structure at 528 eV. This peak indicates transitions to O-2p states which give rise to holes in the valence band. Inset: Z-contrast image corresponding to a [$YBCO_1/PBCO_5$] superlattice. The darker contrast corresponds to YBCO layers (marked with black arrows).

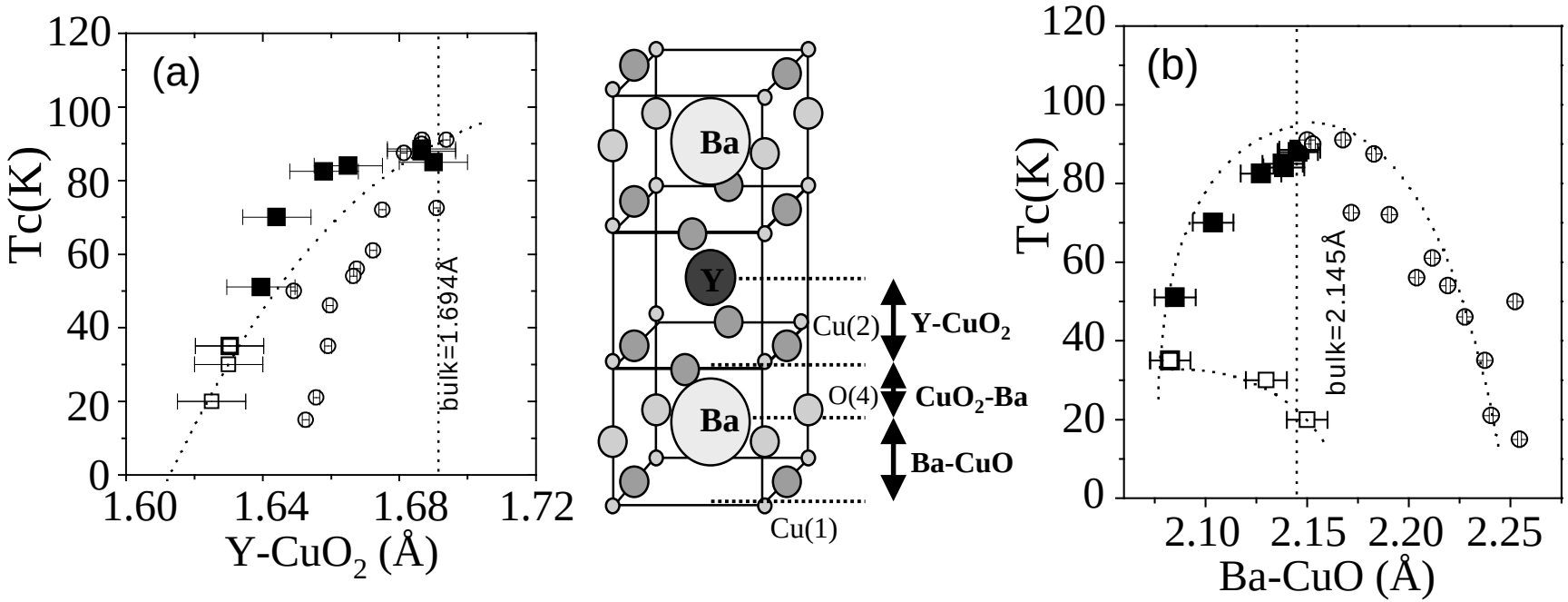

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Figure 1

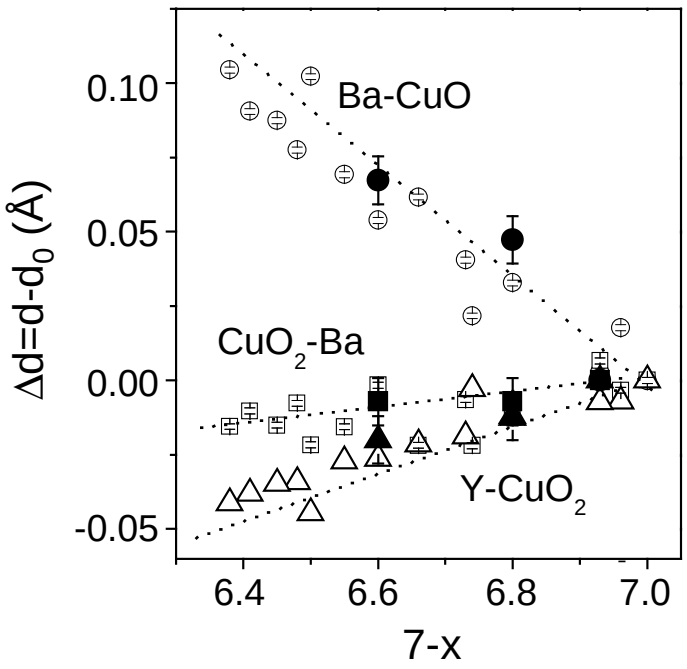

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Figure 2

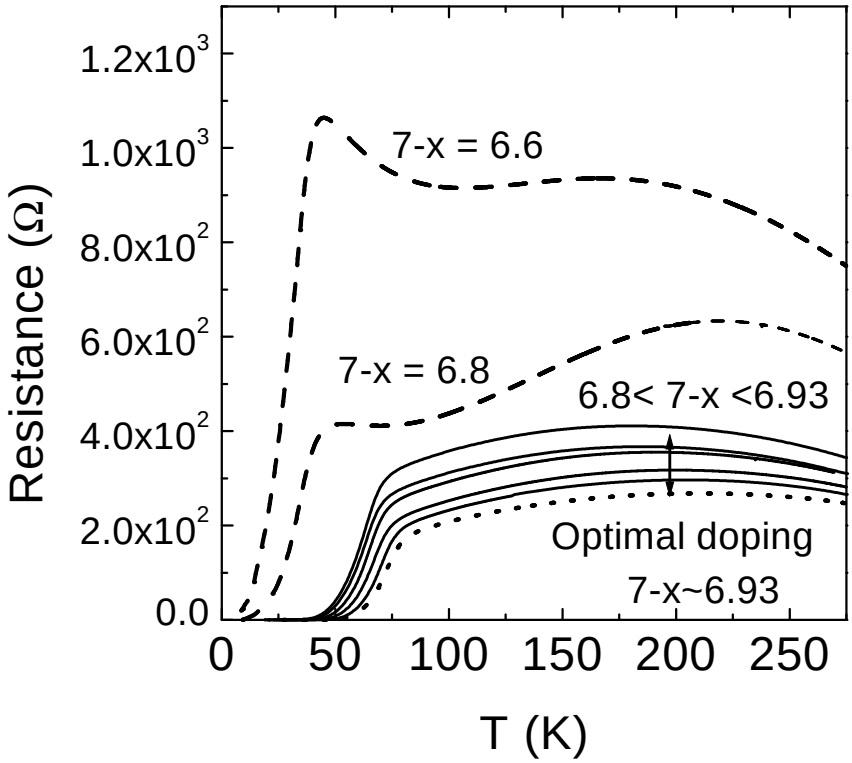

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Figure 3

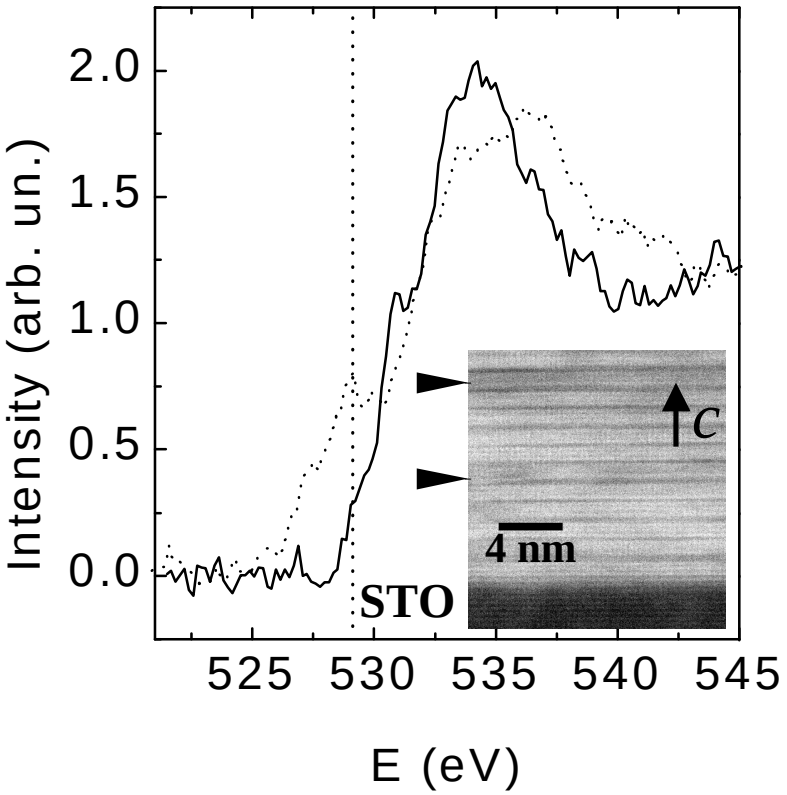

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Figure 4